Yes! More Gibbs!

Temperature Dependence of the Equilibrium Constant and Free Energy
Phase equilibria
Free energy and electrical work

Temperature dependence of K

So last time we were discussing the temperature dependence of the equilibrium constant and the free energy and we came up with two expressions:

$$\boxed{\left(\frac{\partial \Delta\mu}{dT}\right)_P = -\Delta S}$$

$$\boxed{\left(\frac{\partial \ln(K_{eq})}{dT}\right)_P = \frac{\Delta H^\circ}{RT^2}}$$

$$\boxed{\left(\frac{\partial \ln(K_{eq})}{d(1/T)}\right)_P = -\frac{\Delta H^\circ}{R}}$$

This last equation when integrated gives:

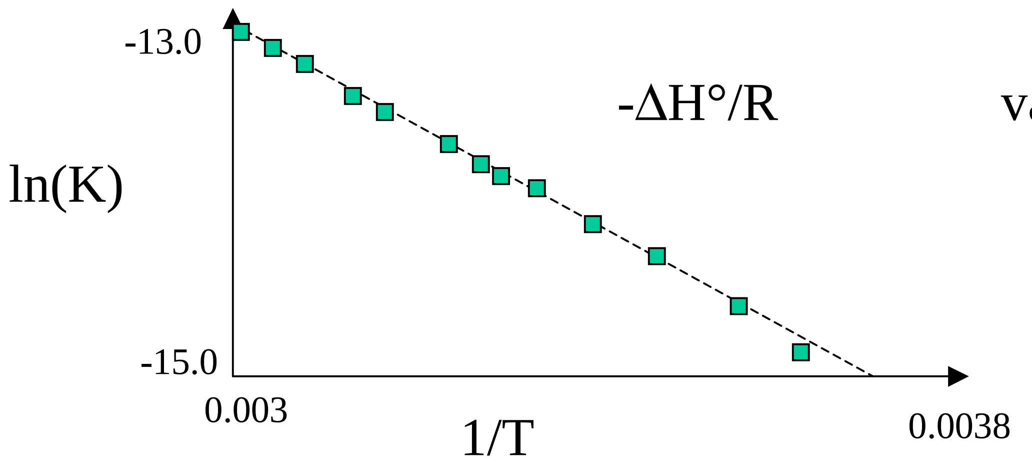
$$\ln\left(\frac{K_2}{K_1}\right) = -\frac{\Delta H^\circ}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

Assuming ΔH° is temperature independent.

Temperature dependence of K

What this means is that a plot of $\ln(K_{eq})$ vs. $1/T$ yields an estimate for $\Delta H°$

$$\boxed{\left(\frac{\partial \ln(K_{eq})}{d(1/T)}\right)_P = -\frac{\Delta H°}{R}}$$



van't Hoff plot

Note that the $\Delta H°$ calculated over this range is approximate. An average.

Also note that the equation above is exact (when $\Delta S°$ is temperature independent). Given a functional form for $\Delta H°(T)$ you could integrate this equation for changing enthalpy.

Temperature dependence of K

Let's test our intuition with an example:

$$2\,CO\,(g) \quad + \quad O_2\,(g) \longleftrightarrow 2\,CO_2(g)$$

The thermodynamic data for this reaction are:

$\Delta G°_{298}$ = -514.4 kJ/mol
$\Delta H°_{298}$ = -566.0 kJ/mol
$\Delta S°_{298}$ = -172 J/K mol

Will the position of the equilibrium constant for this reaction increase, decrease or stay the same upon

(a) an increase in pressure?
(b) an increase in temperature?

Remember that the equilibrium constant for this reaction is extremely large!

Temperature dependence of K

Increasing pressure shifts the equibrium to the right!

$$2\,CO\,(g) \quad + \quad O_2\,(g) \longleftrightarrow 2\,CO_2(g)$$

By LeChâtelier's principle the system moves to decrease the effect of the perturbation.

There are three moles of gas on the left of the equation and two on the right.

The equilibrium will shift towards the more compact form!

Temperature dependence of K

Increasing the temperature:

We are given: $2\,CO\,(g) + O_2\,(g) \quad 2\,CO_2(g)$

ΔG°_{298} = -514.4 kJ/mol
ΔH°_{298} = -566.0 kJ/mol
ΔS°_{298} = -172 J/K mol

Using,

$$\boxed{\left(\frac{\partial \Delta\mu}{dT}\right)_P = -\Delta S}$$

we can see that the chemical potential increases with temperature. So we shift left. This is consistent with:

$$\boxed{\left(\frac{\partial \ln(K_{eq})}{d(1/T)}\right)_P = -\frac{\Delta H^\circ}{R}}$$

which states directly that the equilibrium constant will decrease with increasing temperature when $\Delta H^\circ < 0$!

Note that these two approaches are different. One needs to be careful with the free energy form during sign changes.

Temperature dependence and Acid/Base

Acids and bases can be categorized into roughly five categories:

Strong Acids
Weak Acids
Neutral Species
Weak Bases
Strong Bases

It is difficult to talk about the equilibrium constant for strong acids and bases because they fully dissociate leaving one of the terms in the equilibrium constant very close to zero.

Weak acids and bases only partly dissociate:

$$\underset{\text{Acid}}{HA} \longleftrightarrow \underset{\text{Acid}}{H^+} + \underset{\text{Base}}{A^-}$$

A is the conjugate (or corresponding) base to the acid HA. What is H^+'s conjugate base?

Temperature dependence and Acid/Base

Table 4.1 gives pK_a values for many important biological acids and bases.

Compound	Ionizing Species	pK	ΔH° (kJ/mol)
Acetic Acid	$HOAc \longleftrightarrow H^+ + OAc^-$	4.76	-0.25
Adenosine	$AH^+ \longleftrightarrow H^+ + A$	3.55	15.9
Alanine	$^+H_3NRCOOH^+ \longleftrightarrow H^+ + {}^+H_3NRCOO^-$	2.35	2.9
	$^+H_3NRCOO^- \longleftrightarrow H^+ + H_2NRCOO^-$	9.83	45.2

Most of these ΔH°'s are positive. So

$$\boxed{\left(\frac{\partial \ln(K_{eq})}{dT}\right)_P = \frac{\Delta H^\circ}{RT^2} > 0}$$

Which is consistent with what we found for water!

Odds and ends about Acids and Bases

We can often write something we think of as a base in "acid" form. For example, we normally think of ammonia as a base. But we can write it as follows:

$$NH_4^+ \longleftrightarrow NH_3 + H^+$$

Any of these equilibria can be represented by the Henderson-Hasselbach equation.

$$K_{eq} = \frac{[H^+][A^-]}{HA}$$

$$pK_A = -\log(K_{eq}) = -\left[\log[H^+] + \log\left(\frac{[A^-]}{[HA]}\right)\right] = pH - \log\left(\frac{[A^-]}{[HA]}\right)$$

From here we can relate pK's and pH's and discuss buffering capacities.

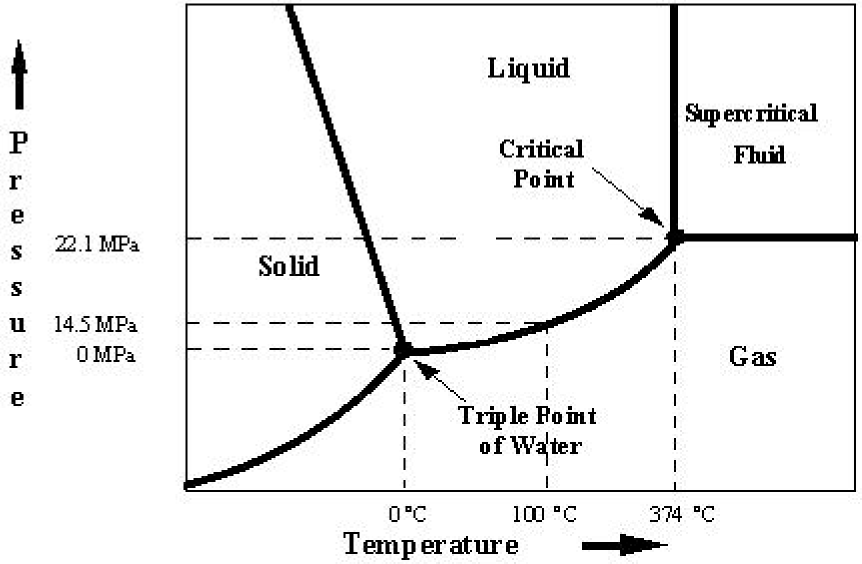
Buffering capacity is the resistant to change in pH upon addition of acid or base. You can prove that buffering capacity increases with concentration and is maximum when $[A^-]=[HA]$.

T-dependence of K and Phase Diagrams

So as we change temperature the equilibrium constant can change. Obviously, if we change temperature enough, we will change phases.

Let's examine now phase diagrams that show this effect:

Phase Diagram for Water

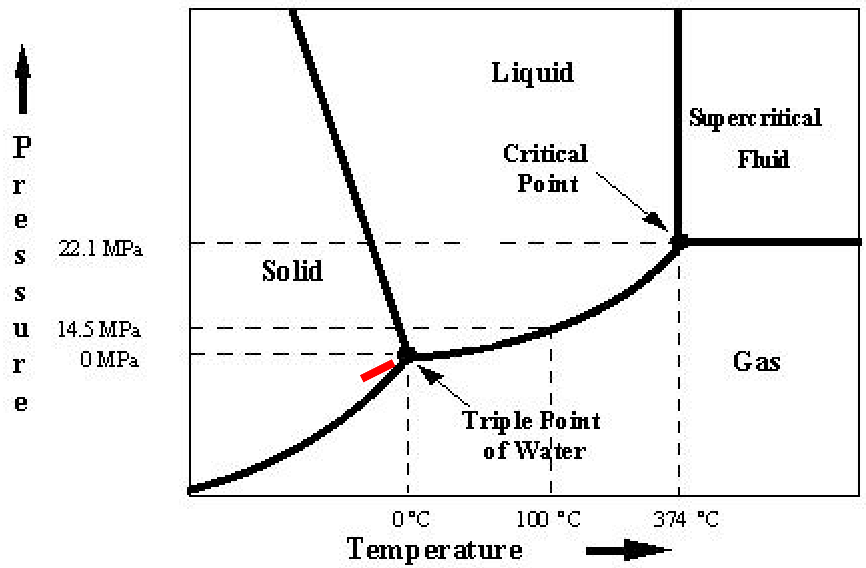


1atm= 101,325 Pa

The black lines are loci of point at which the two (or three) phases of water are in equilibrium.

On either side of the black lines, water enters the pure state.

T-dependence of K and Phase Diagrams



The triple point is the only point at which all three phases exist simultaneously in equilibrium.

At 1 atm water freezes at 0°C.
The triple point occurs at 0.005 °C at a pressure of about 1/200 atm= 4.6 Torr.

This is odd! Usually the triple point is a little below freezing! This occurs because:

$$V_{\text{ice I}} > V_{\text{liquid}}$$

Is it easier to skate on dry ice or water ice? Why?

Temperature dependence of K

Intuitively we know that K will change with temperature. Consider:

$$H_2O \longrightarrow H^+(aq) \quad + \quad OH^-(aq)$$

At 25 °C we know the ionization constant for pure water is $1.01*10^{-14}$M.

If we raise the temperature how should this change?

We should get more ionization, right?

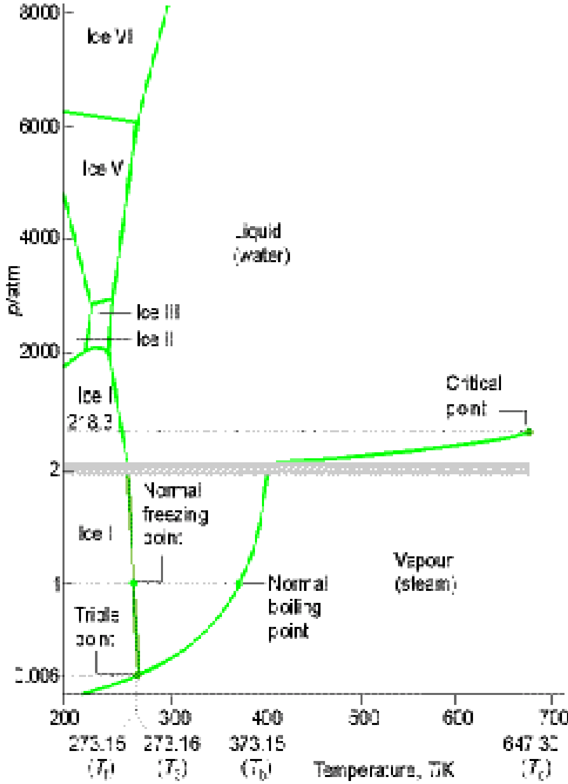
(Heat is released upon mixing acid and base…so heat must be absorbed to dissociate them)

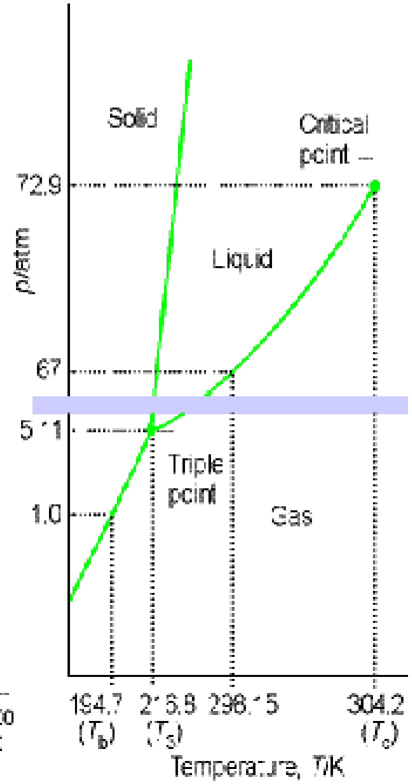
Experimentally, it is found that at 37 °C, $K_w = 2.40 *10^{-14}$M.

Well, we know that the free energy changes with temperature:

$$\boxed{\left(\frac{\partial \Delta\mu}{dT}\right)_P = -\Delta S}$$

The extremes of the phase diagram

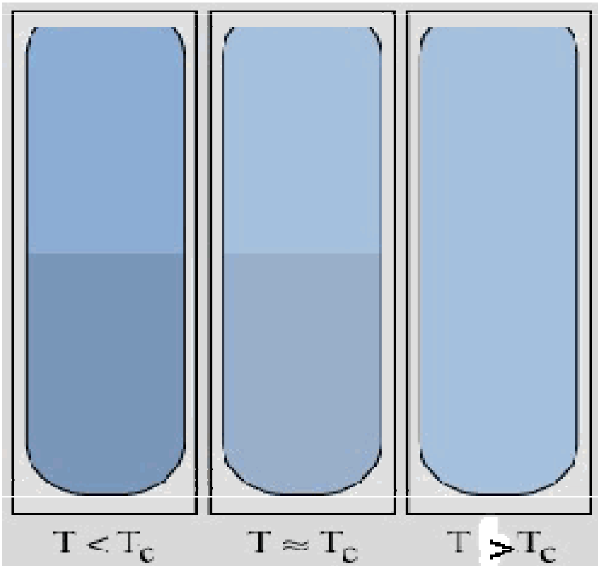


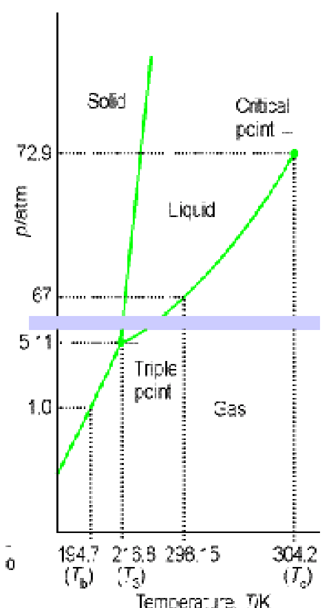


At high pressures and low temperatures ice can rearrange itself into more and more compact forms (Ice II- Ice VIII).

At the critical point the distinction between liquid and gas phases disappears

The extremes of the phase diagram





At the critical point the densities of the gas and liquid become the same.

The meniscus disappears; neither liquid nor gas formally exist.

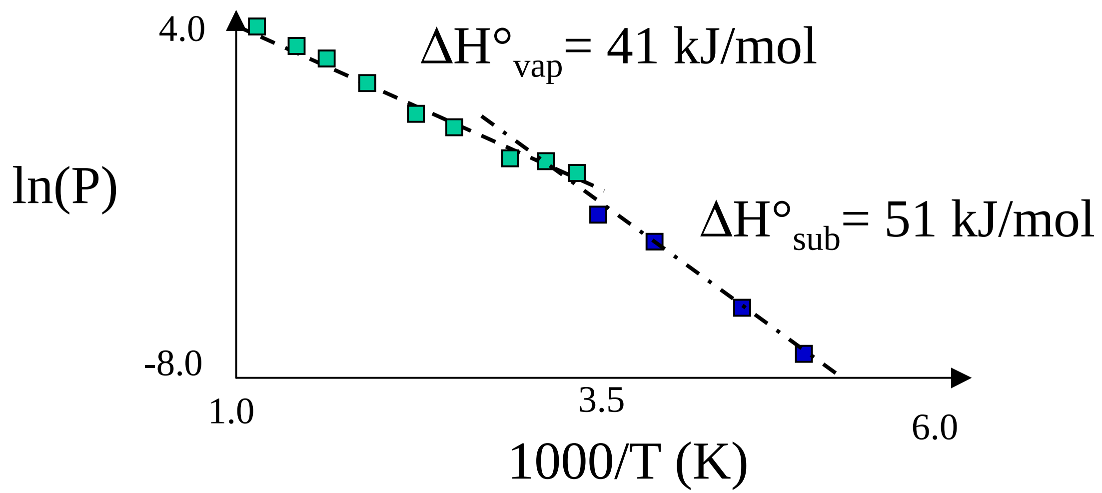
For water the critical point is 374 °C at 217.6 atm
Its molar volume is 56 cm^3/mol (vs. 18 cm^3/mol at room temperature!).

The critical point can be very useful. Above the critical point CO_2 becomes a so-called critical fluid.

This is a useful solvent for caffeine and other alkaloids from coffee-- and the temperature and pressure aren't high enough to damage the coffee itself! (And no chlorinated solvents!)

More Temperature Dependence

Now, back to water phase diagrams. We can derive ΔH for vaporization and sublimation from plotting ln(P) vs. 1/T much like the van't Hoff plot!



From the book (Table 2.2) we find that the ΔH°_{vap} at 298K is 40.66.

What's the discrepancy?

Why is is difficult to get ΔH°_{fus} from this sort of experiment?

Calculating Other ΔH°'s.

For one thing its hard to measure the pressure dependence of liquid and solid!

But remember we can combine reactions!

		ΔH° kJ/mol
H_2O (s)	$\longleftrightarrow$ H_2O(g)	51
H_2O (g)	$\longleftrightarrow$ H_2O(l)	-41
H_2O (s)	$\longleftrightarrow$ H_2O(l)	10

But Table 2.2 gives this value as:

$$\Delta H^\circ_{fus} = 6 \text{ kJ/mol at } 0^\circ\text{C}$$

What's the discrepancy?

In any case, many changes in equilibria are measured with this methods.

Galvanic Cells

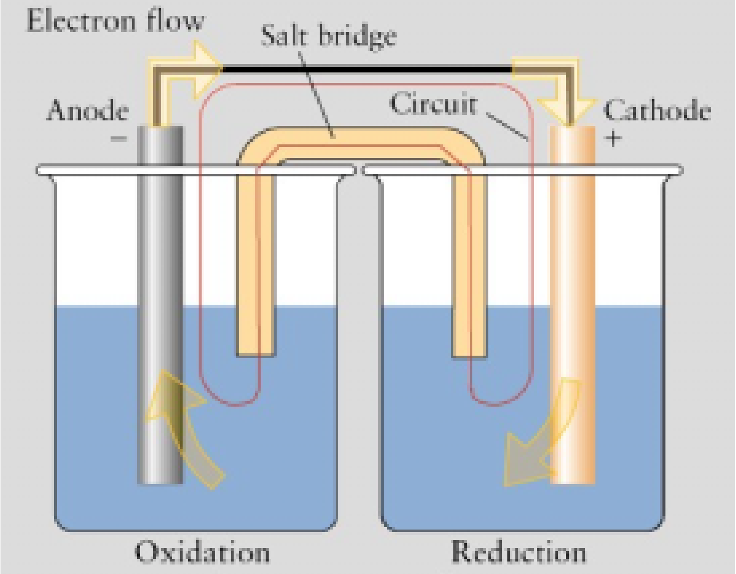
So we've been talking about how to measure thermodynamic properties with changes in temperature and pressure.

We've also been taking for granted that we can get work out of these free energy changes in order to say drive developmental processes.

But there are even more accurate ways to measure free energy changes and this effect also provides an easy method for getting work out of chemical reactions.

This is to run the processes in electrochemical cells. That is to use a system electrically sensitive to the species of interest.

To discuss this we introduce the galvanic cell.



Free energy and electrical work.

To see how free energy relates to electrical work we start with the fundamental equation for G.

$$G = E + PV - TS$$

For a change in G at constant T and P

$$\Delta G = \Delta E + P\,\Delta V - T\,\Delta S$$

If we apply the first law for a reversible process (remember we want maximum work) we get:

$$\Delta G = q_{rev} + w_{rev} + P\,\Delta V - T\,\Delta S$$

$$= w_{rev} + P\,\Delta V \quad \text{(Why?)}$$

Because -P ΔV is the pressure-volume work. We get:

$$\Delta G = w_{rev} - w_{PV} = w_{max,useful}$$

Free energy and electrical work.

$$\Delta G = w_{rev} - w_{PV} = w_{max,useful}$$

In a galvanic cell this is the reversible electrical work!

Now electrical work is simply

$$w_{elec} = \varepsilon * I * t = \varepsilon * \Delta C$$

where ΔC is the amount of charge transferred during the reaction. For n moles of electrons transferred during the course of a reaction we get therefore:

$$\Delta G \text{ (electron volts)} = -n\,\varepsilon$$

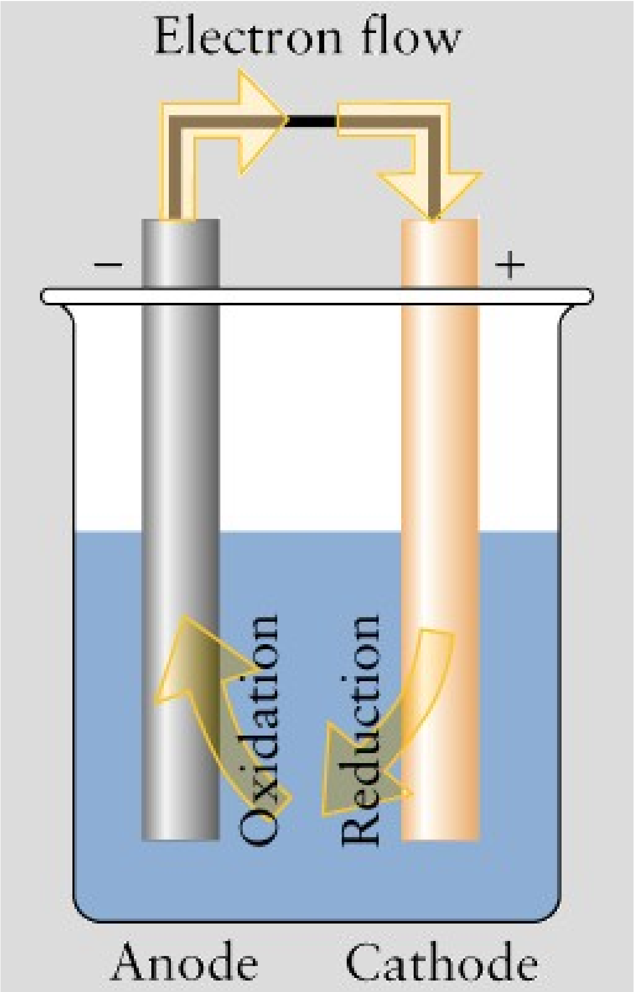
$$\Delta G \text{ (J)} = -n\,F\,\varepsilon$$

where we will discuss the sign convention in a moment and F is Faraday's constant (96,485 coulombs (C) /mol of electrons)

Free energy and electrical work.

It is possible to derive how ΔS and ΔH change with the temperature dependence of

ε but it is straight forward and left to you.



When we talk about electrochemical reactions, we say that they are spontaneous when

$$\Delta G < 0$$

which implies

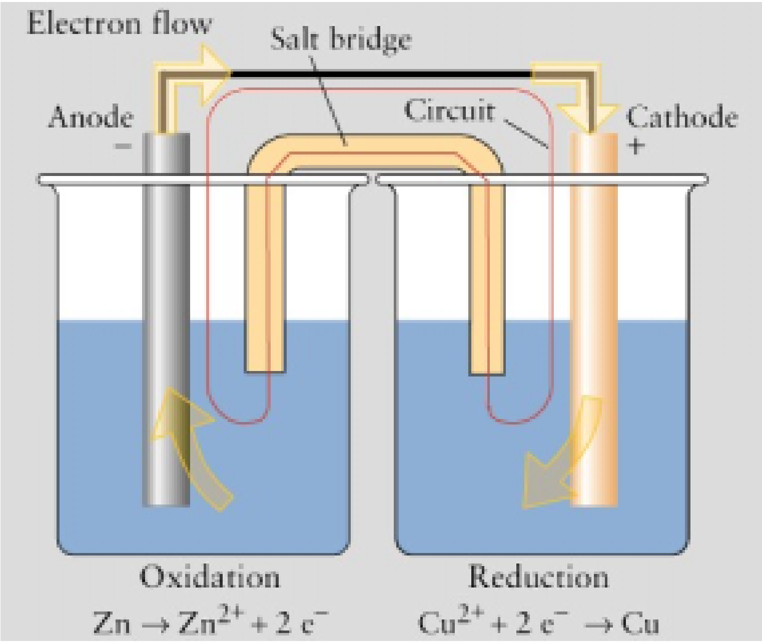
$$\varepsilon > 0$$

Also by convention we right the oxidation reaction occuring at the left electrode.

A useful mnemonic is:

Red-Cat, An Ox

Free energy and electrical work.



In most of the cases we talk about two half-cells. One containing the oxidation reaction and the other containing the reduction reaction.

The salt bridge permits the flow of aqueous ions but prevents real mixing.

We can measure the standard free energy of these reaction using the tables (see Table 4.4)

This particular cell is measuring the reduction of copper by zinc.

$$Zn(s) + Cu^{2+}(a=1) \longleftrightarrow Zn^{2+}\,(a=1) + Cu\,(s)$$

The half cell reactions are: ε° (volts)

$Cu^{2+}(a=1)$	$+ 2$ e-	$\longleftrightarrow$	Cu (s)	0.337
Zn(s)		$\longleftrightarrow$	Zn^{2+} (a=1) + 2 e-2	-(-0.763)

$\varepsilon^{\circ}_{cell} =$ 1.1

Which gives a $\Delta G° = -2.2$ eV = -212 kJ.

Read until end of Chapter 4 , Chapter 5 until page 208

TSW: 4.11,4.14,4.17,4.21,4.30